Visible light-induced photofixation of CO_2 into benzophenone: roles of poly(*p*-phenylene) as photocatalyst and two-electron mediator in the presence of quaternary onium salts

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Visible light-induced photocatalytic fixation of CO_2 into benzophenone (1) has been carried out in CO_2-saturated DMF (*N*,*N*-dimethylformamide) using poly(*p*-phenylene) (PPP) as a heterogeneous photocatalyst and triethylamine as an electron donor. Diphenylglycolic acid (2) is produced as a CO_2-fixed product together with benzhydrol (3), benzopinacol (4) and 1,1-diphenylpropane-1,2-diol (5). The presence of quaternary onium salts such as tetraethylammonium chloride (Et_4NCl) increases the yield of 2 in the presence of CO_2 and those of 3 and 5 in the absence of CO_2. The soft onium cations from quaternary onium salts are proposed to stabilize diphenylcarbinol anion (9) as a common precursor of 2, 3 and 5 on the basis of the HSAB concept. Further, the enhanced formation of PPP dianions (7) through PPP radical anions (6) has been examined in the reduction of PPP with sodium metal in the presence of Et_4NCl. Photocatalysis of PPP in the CO_2 fixation is discussed in terms of onium salt effects and favorable photoformation of 6 and 7 as an electron pool in the presence of quaternary onium cations.

Introduction

Photochemical and electrochemical reduction of CO_2 has been extensively studied in order to develop novel methods for the recycling of CO_2 into useful products from the viewpoint of the role of CO_2 in the greenhouse effect.[1] In natural photosynthesis, CO_2 is fixed to organic substrates by enzymatic reactions using photoformed NADPH as a reducing agent and photoformed ATP as a source of chemical energy. Recent studies on CO_2 reduction have revealed that direct reduction of CO_2 requires a highly negative electron potential (−2.2 V *vs.* SCE),[2] but the electrochemical fixation of CO_2 into benzophenone[3] and the photochemical fixation of CO_2 into a cobalt hydride complex[4,5] can be achieved at a more positive electron potential. Accordingly, photochemical fixation of CO_2 into some organic molecules by using photosensitizers or photocatalysts is an excellent alternative to the direct reduction of CO_2 to HCOOH or CO by the use of visible light.

Many carbonyl compounds are reduced at a more positive electron potential than CO_2. In fact, poly(*p*-phenylene) (PPP) catalyzes the photoreduction of benzophenone (**1**) to benzhydrol (**3**) and benzopinacol (**4**) under visible light irradiation ($\lambda > 400$ nm) in the presence of triethylamine as a sacrificial electron donor.[6] Bearing in mind that diphenylglycolic acid is formed as a CO_2-fixation product when **1** is electrochemically reduced under a CO_2 atmosphere,[3] the authors successfully attempted the photochemical fixation of CO_2 into **1** by using PPP as a photocatalyst and triethylamine (TEA) as an electron donor under visible light irradiation.[7] Interestingly, the addition of quaternary ammonium chloride enhanced the yield of **2** to *ca.* 30%. The reductive formation of **2** requires a two-electron transfer to the substrate with a proton. In the present paper, we propose a new role for PPP as an electron pool for the two-electron transfer in the photocatalysis of PPP on the basis of the detailed studies on PPP-catalyzed photofixation of CO_2 and comparison of the reduction of PPP with sodium metal (Na) in the presence and absence of tetraethylammonium chloride (Et_4NCl).

Results and discussion

Photofixation of CO_2 into benzophenone

Table 1 PPP-catalyzed fixation of CO_2 into benzophenone in the presence of various salts[a]

Run	Additive salt[b]	Conversion of **1** (%)	Yield[c] (%) **2**	**3**	**4**	Total[d]
1	None	100	3	6	37	46
2	Et_4NCl	100	27	4	49	80
3	Et_4NClO_4	100	9	6	32	47
4	$Bu^n{}_4NCl$	97	15	5	37	67
5	$Bu^n{}_4NClO_4$	100	5	5	31	41
6	Et_4PCl	100	24	4	24	49
7	$Bu^n{}_4PCl$	99	19	5	36	60
8	KF+18-crown-6	96	20	5	20	45
9	LiCl	100	5	8	25	38
10	$MgCl_2$	100	2	6	42	50
11	$Mg(ClO_4)_2$	100	1	6	42	49

[a] Irradiated at $\lambda > 400$ nm for 24 h. [b] Each concentration is 40 mM. [c] Yields are calculated on the basis of converted benzophenone. [d] Sum of the yields of **2**, **3** and **4**.

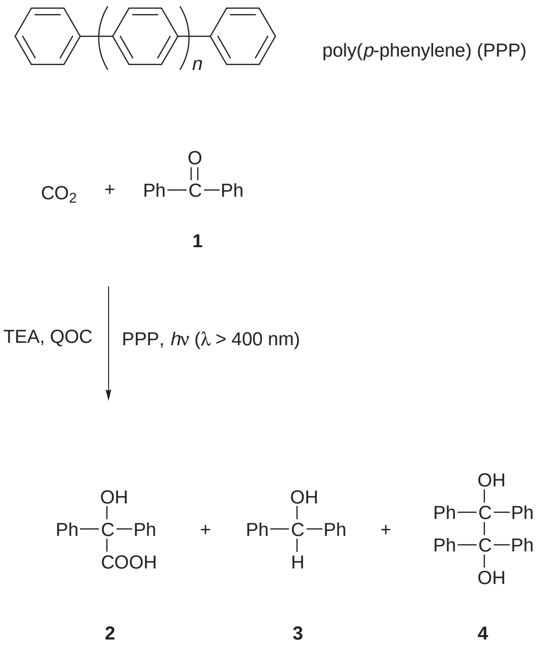
Photoreaction was carried out under visible light ($\lambda > 400$ nm) irradiation of a CO_2-saturated DMF solution containing dispersed PPP, benzophenone (**1**) and TEA (see Table 1). Diphenylglycolic acid (**2**) was formed competitively with benzhydrol (**3**) and benzopinacol (**4**) (Scheme 1) (Table 1). The formation yield of **2** was below 5% and less than those of **3** and **4**. However, the addition of tetraethylammonium chloride (Et_4NCl) to the system improved the yield of **2** to 27%. The apparent quantum efficiency, estimated roughly, was less than 0.01. In the absence of **1** neither CO nor HCOOH was detected as a reduction product of CO_2. As oxidation products, diethylamine and acetaldehyde (MeCHO) were detected during the photoreaction. The formation of these has been attributed to the hydrolysis of a photo-oxidation product of TEA, $[Et_2NCHCH_3]^{+\cdot}$.[6] $^{13}CO_2$ incorporation experiments coupled with ^{13}C-NMR and GC–MS measurements confirmed the photofixation of CO_2 into **1**. The ^{13}C-NMR spectrum was found to contain a signal at $\delta = 175$ ppm attributable[7] to the $^{13}COOH$ group of **2**.

In order to elucidate the salt effect[8] of Et_4NCl on the photocatalysis, the CO_2 photofixation was carried out in the presence of some other organic or inorganic salts (Table 1). Although inorganic salts such as lithium and magnesium salts had almost no effect on the formation of **2** (runs 9–11), the addition

Table 2 PPP-catalyzed photofixation of CO_2 into benzophenone in the presence of MeCHO and/or Et_4NCl[a]

Run	Additive		Conversion of **1** (%)	Yields[b] (%)				
	[MeCHO]/mM	[Et_4NCl]/mM		**2**	**3**	**4**	**5**	Total[c]
1	0	40	99	27	4	49	3	83
2	0	0	97	8	11	69	2	90
3	100	40	98	11	9	40	20	80
4	100	0	98	5	11	36	8	60

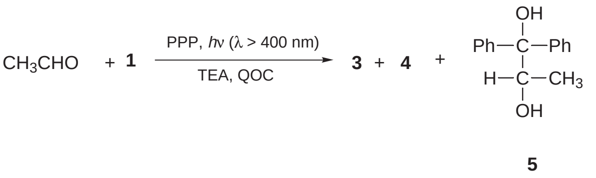
[a] Irradiated at $\lambda > 400$ nm for 24 h. [b] Yields are calculated on the basis of converted benzophenone. [c] Sum of the yields of **2**, **3**, **4** and **5**.



Scheme 1 Photocatalytic fixation of CO_2 into **1** with PPP

of tetrabutylammonium chloride, tetraethylphosphonium chloride or tetrabutylphosphonium chloride gave comparable yields of **2** (runs 4, 6, 7). However, their perchlorates had a poor effect on the CO_2 fixation (runs 3, 5). It is worth noting that the addition of 18-crown-6–KF complex showed a comparable effect with tetraalkylammonium and phosphonium chlorides. 18-Crown-6 complexed with potassium cation can be regarded as a kind of quaternary onium (oxonium) cation, and the cationic charge of potassium ion is delocalized on the oxygen atoms of the crown molecule through ion–dipole interactions. These findings suggest that the presence of appropriate quaternary onium cations (QOC) is essential for the effective production of **2**.

On careful examination of photolysates of the PPP–Et_4NCl–CO_2 system, the formation of 1,1-diphenylpropane-1,2-diol (**5**, racemic mixture) was confirmed by GC–MS and NMR analyses after isolation by gel permeation chromatography. The data obtained for the isolated compound were consistent with those of commercially available (*S*)-(−)-1,1-diphenylpropane-1,2-diol. As reported for the PPP-catalyzed photoreduction of water in the presence of TEA,[9] a very small amount of ethanol was also detected in the present system. These facts suggest that acetaldehyde (MeCHO), which may be formed through photo-oxidation of TEA followed by hydrolysis, participates in the concurrent photoreactions in the system (Scheme 2). In fact, the addition of MeCHO to the system increased the yield of **5** but decreased that of **2** with the formation of a small amount (< 0.3 μmol) of EtOH (Table 2). In the absence of Et_4NCl, however, the addition of MeCHO did not affect the photoreaction to a distinguishable extent (Table 2).



Scheme 2 Photofixation of acetaldehyde into **1**

PPP catalyzes the photoreduction of **1** in the presence of TEA as a sacrificial electron donor, giving **3** and **4** as reported previously.[6] Quaternary onium salts also influenced the photoreduction of **1** in the absence of CO_2 (Table 3). The addition of Et_4NCl increased the formation of **3** and **5** with a decrease in the yield of **4** when compared with those in the absence of Et_4NCl (run 1 *vs.* 2). The addition of both Et_4NCl and MeCHO increased the formation of **5** with a decrease in the yield of **3** (run 1 *vs.* 3) as observed in the presence of CO_2 (Table 2, run 1 *vs.* 3). In the absence of Et_4NCl, the product distribution was not influenced by the addition of MeCHO (run 2 *vs.* 4). The addition solely of MeCHO resulted in a decrease in the total yields of the products derived from **1**, possibly due to the competitive reduction of MeCHO (run 4).

From these observations, we predicted that **2**, **3** and **5** should be produced by the reaction of a common intermediate with CO_2, H^+ and MeCHO, respectively and that the formation of the common intermediate is enhanced by the presence of quaternary onium salts like Et_4NCl.

Molecular orbital calculations of quaternary onium cations and intermediary anionic species

According to the hard and soft acids and bases (HSAB) concept,[10] the softness of an acid (acceptor) or a base (donor) is characterized by a large atomic radius, a low effective nuclear charge and a high polarizability. The semiempirical molecular orbital (MO) calculations of tetraethylammonium cation revealed that 44% of its plus charge is delocalized on the four ethyl chains [see Fig. 1(a)], suggesting that it can be regarded as a soft cation. Similarly, the MO calculations of perchlorate anion (ClO_4^-) also suggested that minus charge is delocalized on its four oxygen atoms on ClO_4^- [see Fig. 1(b)], it being softer in character than chloride ion (Cl^-) with a smaller ionic radius. Accordingly, the effective quaternary onium salts can be characterized as a series of salts consisting of soft acids and hard bases. Undoubtedly, 18-crown-6–KF complex is a salt of a soft oxonium acid and a hard fluoride ion base.

MO calculations also indicated that the charge of the anion **9** is delocalized into the phenyl rings, suggesting that **9** is a soft base [Fig. 1(c)]. The radical anion of PPP ($PPP^{\cdot -}$, **6**), which is formed through reductive quenching of the excited PPP, should be a soft anion, when judged from the delocalized charge distribution of the anion from *p*-terphenyl as shown in the MO calculations [Fig. 1(d)]. Therefore we speculated that QOC should interact preferentially with **9** and **6**, influencing the PPP-catalyzed photoreactions of **1**. Laser flash photolysis of *p*-terphenyl showed that the yield of the radical anion formed through reductive quenching of the excited PPP with triethylamine increased by a factor of 1.2 compared with that in the absence of Et_4NCl.[11] It was also observed that *p*-terphenyl-catalyzed CO_2 reduction under UV irradiation became more efficient in the presence of Et_4NCl than in its absence.[11] In other words, soft QOC coupled with hard bases like Cl^- and F^-

Table 3 Effect of MeCHO and/or Et_4NCl on PPP-catalyzed photoreduction of benzophenone[a]

Run	Additive [MeCHO]/mM	 [Et_4NCl]/mM	Conversion of **1** (%)	Yields[b] (%) **3**	 **4**	 **5**	 Total[c]
1	0	40	100	21	26	27	74
2	0	0	100	15	53	4	72
3	100	40	100	9	23	34	66
4	100	0	100	11	37	11	59

[a] Irradiated at $\lambda > 400$ nm for 24 h. [b] Yields are calculated on the basis of converted benzophenone. [c] Sum of the yields of **3**, **4** and **5**.

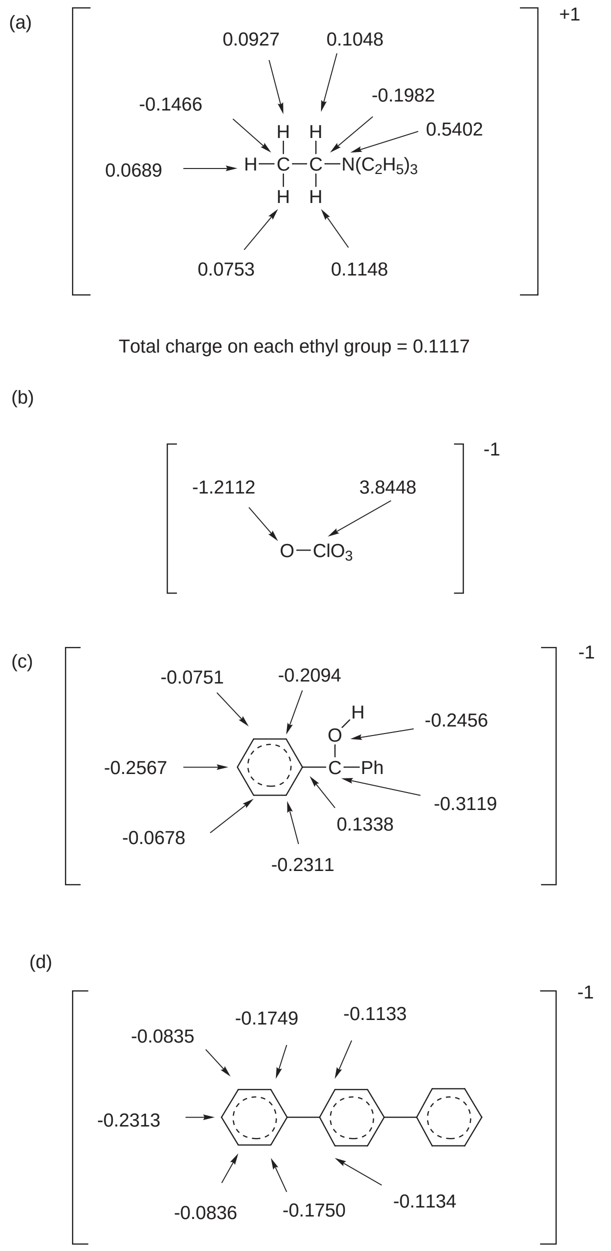


Fig. 1 Charge distributions on (a) Et_4N^+, (b) ClO_4^-, (c) the anion **9** and (d) the radical anion of PPP **6** calculated by the semiempirical MO method (MNDO/PM3)

should prefer to bind with soft **6**, resulting in elongation of the lifetime of **6** and enhancing the electron transfer from **6**.

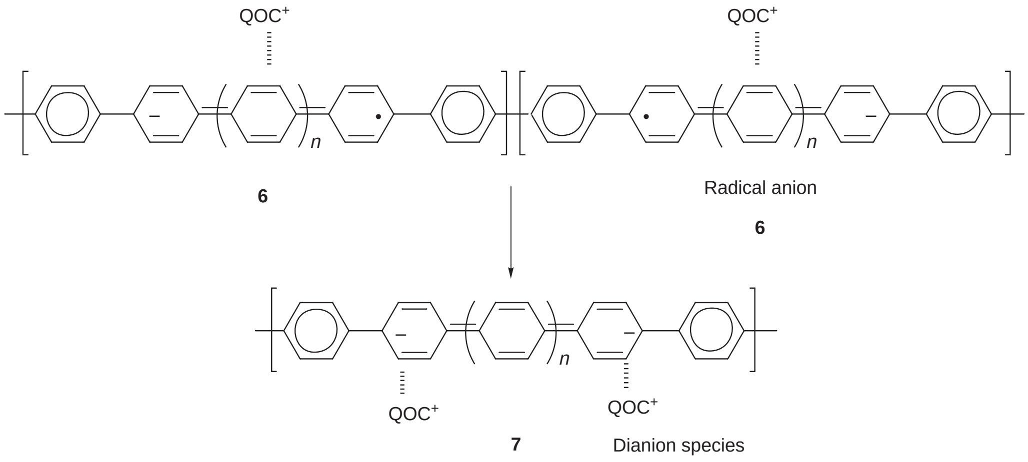
Reduction of PPP with sodium metal in the presence of tetraethylammonium chloride

We assumed that the enhanced formation of **6** and the elongation of its lifetime by interaction with QOC might lead to the formation of PPP dianions (**7**) (denoted as a bipolaron state of PPP in the field of conducting polymers)[12] as shown in Scheme 3. It was reported that the reduction of oligomeric PPP such as *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl and *p*-sexiphenyl with sodium metal (Na) leads to the preferential formation of their dianions through their radical anions in THF. In their EPR measurements, signals due to the radical anions observed at the earlier stage of the reduction had a tendency to disappear on further exposure to sodium metal (longer than 2 h), which is rationalized as due to the formation of their dianions as a two-electron pool.[13]

With these facts in mind, we performed the reduction of PPP with sodium in a similar manner. A dark purple suspension was obtained by the reduction of PPP with Na mirror in THF under ultrasonication. A sharp EPR signal was observed with a *g*-value of 2.122 (see Fig. 2). The intensity of the signal increased during the short exposure time, but decreased to 1/3 of the maximum value on longer exposure to Na metal (Fig. 2). When Et_4NCl was present in the suspension, the rise of the signal became steeper at the initial stage and longer exposure to Na mirror, *i.e.* further reduction, decreased the signal more remarkably than the absence of the added salt (Fig. 2). These facts suggest that the PPP radical anions (**6**) formed by the reduction with Na at the initial stage should undergo further electron transfer from Na, giving preferentially PPP dianion species (**7**), and the formation of **7** is enhanced by the presence of Et_4NCl (Scheme 3). The decrease in the spin density of alkali metal-doped PPP with the increase of the doping level has already been reported and was ascribed to the formation of the dianion species (it is denoted as the bipolaron therein).[14–16]

The formation of PPP dianion species (**7**) was also confirmed by the absorption spectrum of the same sample as used in the above EPR measurements (Fig. 3A). When insoluble PPP was ultrasonicated with sodium in THF, the reduced (Na doped) PPP became soluble to an appreciable extent where the spectra could be measured. The absorption peak observed around 300 nm in the spectrum before the ultrasonication indicates that oligomers such as *p*-terphenyl and *p*-quaterphenyl contained in PPP became dissolved into THF at the initial stage. When the sample was further exposed to sodium, a broad absorption band with peaks around 470 to 520 nm was raised, which is attributed to the radical anions because of the similarity to the reported absorption spectra of the radical anions derived from the oligomers.[9,17–19] Further exposure longer than 20 min brought about two broad bands below 300 nm and above 700 nm followed by a decrease in the absorption band attributed to the radical anions. The baselines of the spectra were gradually raised up as the reduction proceeded. When PPP was reduced to a large extent by long exposure, the solution looked like a homogeneous solution having a dark purple–blue color. The anionic species formed in the PPP chain might make the PPP aggregates loose by Coulomb repulsion, resulting in enhancement of the solubility.

The effects of Et_4NCl on the reduction of PPP with sodium should be emphasized. Interestingly, the presence of Et_4NCl led to the rapid decrease of the EPR signal after an initial steep increase of the signal due to the formation of the radical anions when compared with those in the absence of Et_4NCl (Fig. 2). The enhanced conversion of the radical anions to the dianions was also confirmed by a change in the absorption spectrum



Scheme 3 Photoformation of dianion species through PPP radical anion

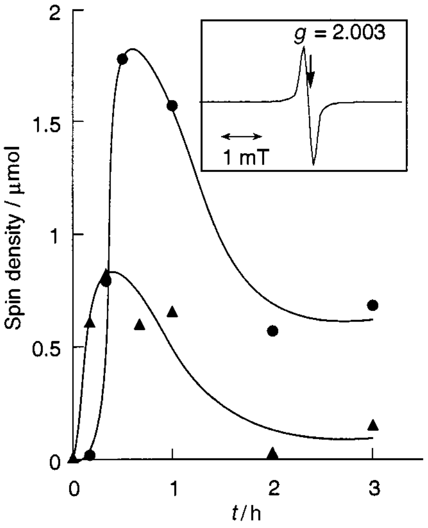


Fig. 2 Change in the intensity of the EPR signal of $PPP^{\bullet -}$ formed through Na reduction under ultrasonication in THF; in the absence (●) and the presence (▲) of Et_4NCl. The inset shows an EPR spectrum observed for PPP reduced with Na by ultrasonication for 30 min.

(Fig. 3B). The dark purple coloration occurred much more rapidly in the presence of Et_4NCl than in its absence. Bearing these facts in mind, it is now concluded that the presence of Et_4NCl should contribute to the rapid Na doping of PPP, enhancing the formation of PPP dianion species through the interaction of triethylammonium cation as a soft QOC.

Reaction mechanism

Assuming that electron and hole pairs (e_{CB} and h_{VB}) are formed on irradiated PPP,[6,9,11] the observed photofixation reactions in the PPP–QOC–TEA system can be depicted as in Scheme 4.[6,20,21]

Photoformed h_{VB} on PPP oxidizes TEA to the TEA radical cation, which undergoes deprotonation, giving *N*,*N*-diethylamino-1-ethyl radical. Since the radical has an oxidation potential of −1.12 V *vs.* SCE in acetonitrile,[22] it can be further oxidized to the iminium cation $[Et_2NC^+HCH_3]$ by h^+_{VB}, producing acetaldehyde and diethylamine through its hydrolysis. Photoformed electron (e_{CB}) on PPP, which can be depicted as the delocalized PPP radical anion (**6**), reduces the ketone **1** to give the intermediary hydroxyl radical **8** through protonation.[23] Pinacol **4** is produced as the dimer of the one-electron transfer reduction intermediate **8** (Scheme 4). The radical **8** undergoes further reductive electron transfer giving the anion **9**, which we postulated as the common intermediate giving **2**, **3** and **5** through reactions with CO_2, H^+ and MeCHO, respectively. The

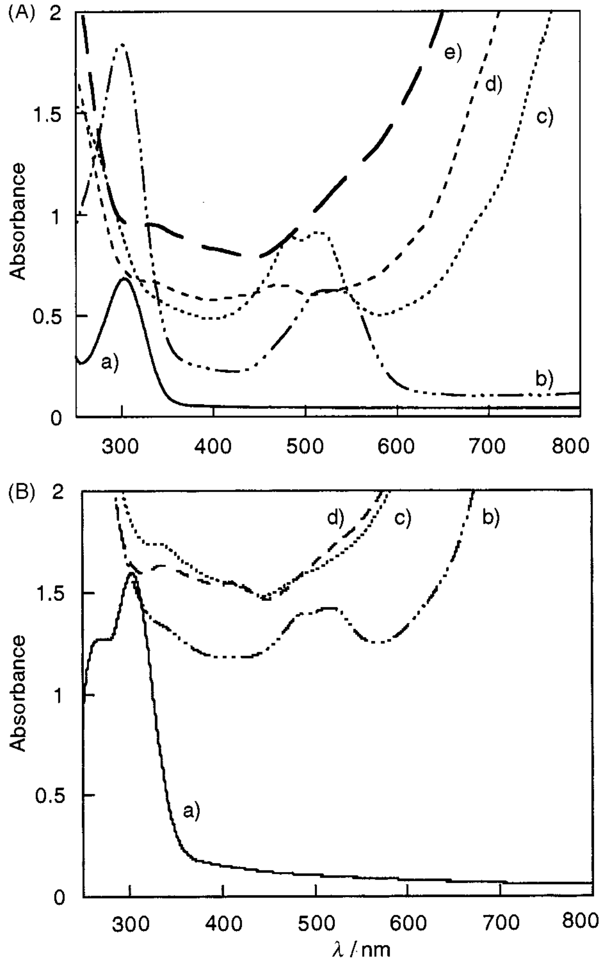
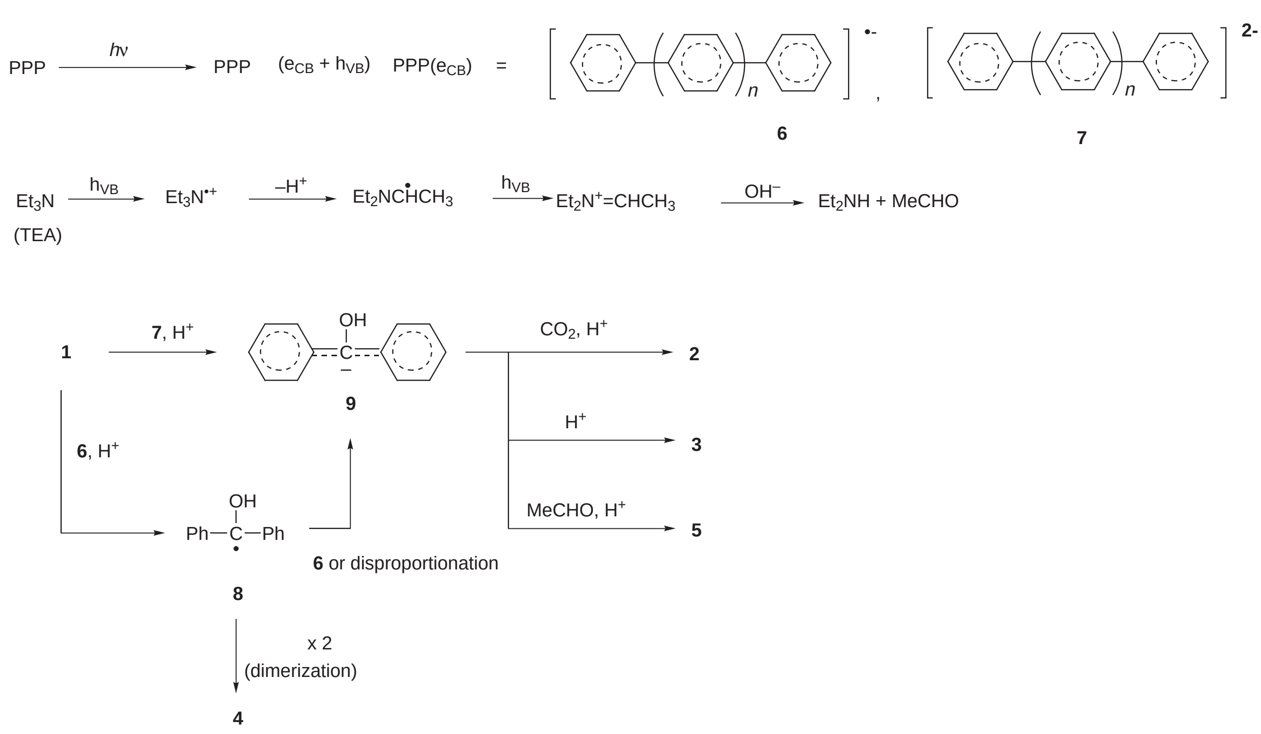


Fig. 3 (A) Change in the absorption spectra of the same solution observed by EPR in the absence of Et_4NCl. Ultrasonication time: (a) 0 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 3 h. (B) Change in the absorption spectra of the same solution observed by EPR in the presence of Et_4NCl. Ultrasonication time: (a) 0 min, (b) 10 min, (c) 20 min, (d) 3 h.

formation of **2** through coupling of the radical **8** with intermediary one-electron reduced CO_2 ($CO_2^{\bullet -}$) was disregarded because CO_2 itself never undergoes direct reduction under visible light irradiation by PPP.[7,11]

The ketyl radical **8** may undergo either disproportionation or coupling as competitive processes to give **3** and **4**. The presence of quaternary onium salts, however, may not affect the disproportionation process because, in the presence of any onium salts, the dimer **4** was formed increasingly with the increased total yield of the products *via* the intermediate **9**. Accordingly,



Scheme 4 Mechanism of the photocatalysis

one role of QOC with harder anions such as chloride and fluoride is ascribed to the enhanced nucleophilicity of the soft common intermediate **9** through their soft–soft interaction (the HSAB concept).

The reductive quenching of the excited PPP with TEA should yield the soft electron supplier **6**, which is regarded as photo-doping of PPP comparable with the doping with sodium. We have revealed that the presence of Et_4NCl enhanced the formation of the soft radical anion (**6**) and its conversion to the dianion species (**7**) in the Na doping (the reduction with sodium). Considering these facts with the HSAB concept, we propose that soft QOC might also contribute to the formation of **6** and **7** in the photocatalysis of PPP as observed in the reduction of PPP with Na (Scheme 3). Since the reductive fixation of CO_2 into **1** requires two-electron transfer, the effective formation of **7** through effective interaction of QOC with **6** explains well the alternative two-electron transfer to **1** yielding of the common intermediary anion **9**.[24]

Conclusions

The PPP-photocatalyzed CO_2 fixation reported in this work is the first known case where CO_2 is reductively converted into useful compounds under visible light irradiation by organic photocatalysts. PPP particles play important roles as an organic photocatalyst and an electron mediator for two-electron transfer in producing organic carbanions to which CO_2 is readily fixed. CO_2 fixation to reduced organic compounds is a promising strategy for harvesting solar energy, since it requires a less negative electron potential than does direct CO_2 reduction.

Experimental

General methods

GC–mass analysis was conducted on a JEOL JMS-DX instrument. ^{1}H-NMR data were obtained on a JEOL JNM-GSX 270 spectrometer. UV–VIS spectra by reflectance spectrometry were recorded on a Photal (Otsuka Electronics) instrument with a spectro-multichannel photodetector (Model MCPD-100). EPR measurements were performed with a JEOL JES-RE2X (X-band) EPR spectrometer. Chemical shifts are given in ppm and *J* values in Hz.

Materials

1,4-Dibromobenzene (over 98% pure), magnesium [guaranteed reagent (GR) grade], tetra-*n*-butylammonium chloride [chemically pure (CR) grade], tetraethylammonium perchlorate (GR), 18-crown-6 (GR), lithium chloride (GR), toluene (EP) and *N*,*N*-dimethylformamide (spectra grade) were obtained from Wako Pure Chemical Industries. Benzophenone (GR), benzhydrol (GR), benzopinacol (GR), diphenylglycolic acid (GR), tetraethylammonium chloride (polarographic grade), potassium fluoride (GR), magnesium perchlorate (GR) and magnesium perchlorate (GR) were purchased from nacalai tesque. (*S*)-(−)-1,1-Diphenylpropane-1,2-diol, tetraethylphosphonium chloride and tetra-*n*-butylphosphonium chloride were obtained from Aldrich Chemical Co. Tetra-*n*-butylammonium perchlorate was purchased from Fluka. The above reagents were used without further purification. TEA was distilled over potassium hydroxide under an argon atmosphere. Methanol was distilled in the presence of magnesium methoxide. THF was distilled over benzophenone-ketyl with sodium. $Ni(bpy)Cl_2$ (bpy = 2,2′-bipyridyl) was prepared from $NiCl_2$ and 2,2′-bipyridine according to the reported method.[25]

Preparation of PPP

PPP was prepared according to literature methods.[26,27] The Grignard reagent obtained from 1,4-dibromobenzene and magnesium (mol ratio 1 : 1) was polymerized in THF in the presence of $Ni(bpy)Cl_2$ as a polymerization catalyst, giving crude PPP. The resulting polymer was thoroughly washed with methanol containing aqueous HCl (volume ratio 9 : 1) and then washed with methanol. The solid was treated with hot toluene in a Soxhlet apparatus and then vacuum-dried at room temperature (Found: C, 81.98; H, 4.85; Br, 11.55%). The absorption spectrum by reflectance spectrometry was consistent with that reported.[6]

Photoreactions

A DMF solution (2 ml) containing PPP (10 mg), benzophenone (2.5 mM), the salt (40 mM, *e.g.* Et_4NCl), and TEA (1 M) was placed into a Pyrex-glass tube (8 mm in diameter). After the mixture was purged with argon, the reaction mixture was saturated with CO_2, the tube was closed off with a gum stopper and then irradiated for 24 h under stirring at $\lambda > 400$ nm using a

300 W halogen–tungsten lamp with a sodium nitrite solution filter.

With regard to the photofixation in the system 18-crown-6–KF, the following procedure, different from the above, was undertaken: PPP was dispersed in a methanol solution containing potassium fluoride (80 μmol) and 18-crown-6 (80 μmol). To the residual solid obtained after methanol was evaporated from the dispersion solution a DMF solution (2 ml) containing benzophenone (2.5 mM) and TEA (1 M) was added. The resulting dispersion solution was supplied to the photoreaction after being saturated with CO_2. After photoreaction, the reaction mixture was directly analyzed by HPLC as described below.

Diphenylglycolic acid was identified as the major product from the coincidence of the HPLC retention time and the absorption spectrum recorded by the detector of the HPLC instrument with those of the authentic sample purchased from nacalai tesque. Analysis of diphenylglycolic acid and 1,1-diphenylpropane-1,2-diol was carried out by HPLC using a Wakosil-II column (4.6 × 150 mm) and a photo-diode array detector (Hitachi Model L-3000) with a mixture of acetonitrile and buffered aqueous solution (KH_2PO_4–NaOH; pH = 7) as an eluent. 1,1-Diphenylpropane-1,2-diol was isolated by gel permeation chromatography (GPC) with JAIGEL 2H and JAIGEL 1H columns on a Nippon Bunseki Kogyo Model LC-908 instrument using chloroform as an eluent and its analytical data were compared with those of authentic (*S*)-(−)-1,1-diphenylpropane-1,2-diol purchased from Aldrich. The analytical data of the isolated compound are as follows: $\delta_H(CDCl_3)$ 1.12 (d, *J* 6.2, 3H), 1.85 (s, 1H), 2.98 (s, 1H), 4.83 (m, *J* 6.2, 1H), 7.15–7.45 (m, 8H), 7.62 (d, 2H). The NMR spectrum also contained other peaks due to remaining Et_4NCl. GC–MS (EI): *m*/*z* 183 [$(M - CH_3CHOH)^+$, 43%], 105 ($C_6H_5CO^+$, 100%), 77 ($C_6H_5^+$, 85%). Benzophenone, benzhydrol and benzopinacol were analyzed by HPLC using a Cosmosil-ODS column (4.6 × 150 mm) and a UV detector (TOSOH Model UV-8000) with a mixture of methanol and buffered aqueous solution (KH_2PO_4–NaOH; pH = 7) as an eluent. Analysis of formate (HCO_2^-) was performed by ion exchange chromatography using a TSK gel SCX(H^+) column (7.8 × 300 mm) at 313 K and a UV detector (TOSOH Model UV-8011) with aqueous phosphate solution (2 mM) as an eluent.

$^{13}CO_2$ incorporation experiments

The photoreactions were carried out under $^{13}CO_2$ in the same manner as described above. ^{13}C-NMR of the reaction solution was measured to confirm the formation of the CO_2-fixation product.

EPR and UV–VIS absorption measurements

The dispersion solution (2 ml) of PPP (1.5 mg) in dried THF was brought into contact with Na mirror under vacuum and ultrasonicated to promote reduction of PPP with Na metal. For each measurement, the dispersion solution was transferred to an attached EPR tube without exposure to the air. The spectrum was measured at room temperature under the following conditions: magnetic field, 336 ± 25 mT; field modulation width, 0.32 mT; microwave power, 4 mW. The relative intensities of the signals were determined using a signal of Mn^{2+}–MgO as a standard. UV–VIS absorption spectra of the dispersion solution were measured by transferring the solution into an attached quartz rectangular cell (10 mm in optical length) *in vacuo*.

Molecular orbital calculations

Semiempirical molecular orbital (MO) calculations were done by MOPAC Ver. 6.10[28–31] using the molecule modeling system (Molgraph, Daikin Co.) installed in a workstation (COMTEC, 4DRPC). The geometries of the molecules were optimized energetically using MNDO/PM3.

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